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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

Releasable

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OFFICE OF
PESTICIDES AND TOXIC SUBSTANCESMEMORANDUM

Subject: PP#2E2706/2H5354. Linuron in or on Sugar Beets: Evaluation of Residue Data and Analytical Methodology.

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Thru: Charles L. Trichilo, Chief *CT*
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To: Hoyt Jamerson, PM 43
Registration Division (TS-767)

and

Toxicology Branch
Hazard Evaluation Division (TS-769)

The IR-4 National Director, on behalf, of the IR-4 Technical Committee and the Agricultural Experiment Station of California requests the establishment of the following tolerances for residues of the herbicide linuron (3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea):

<u>Commodity</u>	<u>Proposed Tolerance</u>
Sugar beet roots	0.2 ppm
Sugar beet tops	1.0 ppm
Dried sugar beet pulp (food additive)	1.0 ppm

Tolerances have already been established for residues of linuron on various raw agricultural commodities ranging from 0.25 ppm to 5 ppm. Included in these commodities are vegetables, grains and meat and meat by-products of cattle, goats hogs, horses and sheep. Temporary tolerances were established (PP#6G1791) for linuron in or on sugar beet roots at 0.2 ppm and sugar beet tops at 1 ppm in connection with an experimental use permit which expired in 1975. Also, a food additive regulation was established for residues of linuron on dried beet pulp at 1 ppm concurrent with the same permit.

A letter of authorization was submitted in this petition, authorizing EPA to refer to DuPont data on linuron when considering this tolerance proposal.

Formulation information deleted from page 4.

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INTERNATIONAL RESIDUE LIMIT STATUS

CHEMICAL Linuron

PETITION NO FE2700/245354

CCPR NO. none

Revised: Jan E. 1964

Codex Status

Proposed U. S. Tolerances

☒ No Codex Proposal
Step 6 or above

Residue (if Step 9): _____

Residue: Linuron

Crop(s) Limit (mg/kg)

Crop(s) Tol. (ppm)

Sugarbeet roots 0.2
Sugarbeet tops 1.0
Dried sugarbeet pulp 1.0

CANADIAN LIMIT

MEXICAN TOLERANCIA

Residue: _____

Residue: _____

Crop Limit (ppm)

Crop Tolerancia (ppm)

none (on sugarbeets)

none

Notes:

Minor Use Considerations

IR-4 submits this petition for consideration by the Agency as a minor use petition. They indicate in the directions for use that the use of linuron is restricted to Arizona, California and New Mexico. This restriction is imposed because of the limited residue data available.

We do not consider the use of linuron on sugar beets as a minor use. According to USDA Agricultural Statistics 1979, U.S. Government Printing Office, Washington (1979), 1.3 million acres of farmland in the U.S. were planted to sugar beets in 1979 and the value of the yield was more than 0.6 billion dollars. The production in the states listed above to which this use would be limited account for approximately 26% of this total production (0.16 billion dollars). Such statistics, in our judgment, constitute a major crop and a major use. Consequently, our review of this petition is based on the judgment that the use of linuron on sugar beets is not a minor use.

We should also point out that the earlier temporary tolerance petition was submitted by E.I DuPont Co. At that time, several data requirements were outlined for a permanent tolerance. These included additional residue data for sugar beet roots, tops, molasses and sugar and indicated the need for a milk tolerance. None of the data deficiencies cited in the temporary tolerance petition, as deficiencies needing to be answered before a permanent tolerance could be established, have been addressed in this petition from the IR-4.

Conclusions

1a. The nature of residue in plants is adequately understood. The residue of concern is the parent compound.

1b. The nature of the residue in animals is adequately understood. Little residue of linuron per se is expected in tissues and/or milk. Metabolites expected to occur in tissues and/or milk are 3,4 dichlorophenyl methyl urea, 3,4-dichlorophenyl urea and 3,4-dichloroaniline. These residues are determined by the analytical methodology.

2. Adequate analytical methodology is available for enforcement of the proposed tolerances. Bound residues are determined by the method.

3a. As discussed above, we do not consider this petition to be a minor use. We can draw no conclusion on the level of residue that is to be expected in sugar beets (roots and tops) from the proposed use because of the limited amount of data submitted.

Residue data are needed from the Rocky Mountain States, Great Plains and North Central States in order to draw a conclusion on the level of residue expected in treated beets.

3b. For the data submitted as well as the data requested in conclusion 3(a) above, raw analytical data and information are needed such as:

(a) sample chromatograms for G.C. determinations and standard curve and plots for colorimetric determinations (b) information on time between sampling and analysis and (c) storage stability data if samples are stored for a long period.

3c. Additional residue data are needed for dried sugar beet pulp. Residue data are also needed for sugar and molasses. The dried beet pulp, sugar and molasses should be derived from beets bearing residues at or near the proposed tolerance level. If residues are concentrated in these processed commodities, appropriate food additive tolerances should be proposed.

4a. The tolerances already established for the meat, fat and meat by-products of cattle, goats, hogs, horses and sheep are adequate to cover secondary residues in these commodities resulting from the proposed use as well as the already registered linuron uses. Note: The topical discussion for the RCB part of the linuron Registration Standard suggests a downward revision for these meat tolerances (except liver and kidney). However, we are not making this consideration an issue in our review of this petition.

4b. With respect to poultry tissue and eggs, the proposed use falls into Sec. 180.6(a)(3).

4c. In our earlier review for the temporary tolerances, we concluded that the residue data for milk indicated that a milk tolerance was necessary. We reiterate this conclusion. An appropriate milk tolerance should be proposed. Enforcement methodology should also be submitted.

Recommendations

We recommend against the proposed tolerance because of conclusions 3a, 3b, 3c, and 4c. For a favorable recommendation the following requirements should be met:

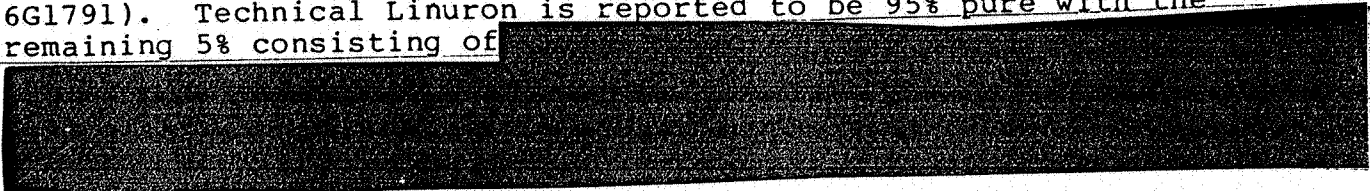
1. Residue data should be submitted for the Rocky Mountain States, Great Plains and North Central States.
2. Appropriate raw data should be submitted showing sample chromatograms for G.C. and standard curves and plots for colorimetric determinations; information on time lapse between sampling and analysis; and storage stability data if samples were stored before analysis.
3. Additional residue data on residues in sugar beet pulp should be submitted.
4. Data should also be submitted for residues in sugar and molasses. The beets used for processing should bear residues at or near the proposed tolerance level. Appropriate food additive tolerances should be proposed if needed.

5. A tolerance should be proposed (with accompanying methodology and feeding study data) for residues in milk.

Detailed Considerations

Manufacturing Process

The manufacturing process for technical linuron has been delineated in earlier petitions for this chemical (See 1E2486, 1E1148 and 6G1791). Technical Linuron is reported to be 95% pure with the remaining 5% consisting of



The impurities in technical linuron are not likely to be a residue problem.

Formulation

Linuron is formulated as Lorox® wettable powder (EPA Reg. No. 352-270) and Lorox®L (EPA Reg. No. 352-391). The wettable powder contains 50% active ingredient and the liquid formulation contains 41% active ingredient (4 lb linuron/gallon). The inert ingredients are all cleared in 40 CFR 180.1001.

Proposed Use

Linuron is to be used to control broadleaf weeds and grasses in sugar beets. It is to be applied as a post emergence lay-by spray at the rate of 1 to 1 1/2 lbs A.I./A. Spray is not to come in contact with foliage and is not to be applied within 3 months of harvest.

There is a restriction that linuron is to be used only in the States of Arizona, California and New Mexico. This restriction is added because of the limited testing geographical area. (Only data for the State of California were submitted.)

Nature of Residue

Plant Metabolism

No metabolism data were submitted with this petition. However, we have considered the metabolism of linuron in previous petitions (PP#413, 7F0542, 1E1148). Metabolism studies were conducted with corn, soybeans and crabgrass. It was determined that linuron is absorbed from the soil, metabolized and translocated by the plants. Metabolism involves demethylation to yield 3-(3,4-dichlorophenyl)-1-methoxyurea followed by demethoxylation and hydrolysis to yield 3,4-dichloroaniline.

Formulation information deleted.

Also, it was noted that 15-25% linuron absorbed in the root uptake study was in the form of "bound" residue at intervals up to 14 days. These bound residues increased with time. This does not present an enforcement problem, however, because of the vigorous hydrolysis step in the analytical method which will release these residues.

Although we have no metabolism data on sugar beets, it is reasonable to assume that the degradation products in sugar beets will be similar to those in the crops on which studies were conducted. We consider the metabolism of linuron adequately delineated in plants. All metabolites of significance are analyzed and reported as parent compound.

Animal Metabolism

No animal metabolism data were submitted.

The topical discussion in the RCB part of the linuron Registration Standard does discuss the available animal metabolism data. Data are available for goats, dogs and rats. It was concluded that the residues of concern are linuron; 3,4-dichlorophenyl methyl urea; 3,4-dichlorophenyl urea; and 3,4-dichloroaniline.

Analytical Method

Two analytical methods were used for residue determinations. A gas chromatographic procedure as described by Imre Baunok and Hans Geissbuehler, Bull. of Env. Contam. and TOX, 3, 7-17 (1968) was used for samples of roots and tops. A colorimetric procedure by H.L. Pease J. Ag. Food Chem. 10, 279-281 (1962) was used for dried pulp and selected samples of roots and tops.

Both procedures involve hydrolysis of the residue under reflux condition in a strongly alkaline medium which quantitatively hydrolyzes linuron to 3,4-dichloroaniline (DCA) while simultaneously partitioning DCA into an organic solvent. DCA is then diazotized and either (1) coupled with ethylenediamine and determined colorimetrically (Pease) or (2) The diazo moiety is exchanged to iodine and the resulting iodinated derivative determined by gas chromatography (Baunok and Geissbuehler).

The recoveries for tops, roots and dried pulp average 102, 100 and 97% respectively.

Adequate analytical methodology is available for determining residues of linuron. An enforcement method is in PAM II, Method I. Also, a paper chromatographic confirmation method is available, PAM Method II. The latter method will distinguish interfering urea herbicides in the colorimetric procedure.

Residue Data

Studies were conducted in the State of California on fall planted sugar beets. Ten plots were used: four in Brawley, CA and six in Calipatria, CA. The crops were treated at lay-by with 1 1/2 and 3 lb linuron per acre (1X and 2X the proposed maximum rate). Samples were collected approximately 90-105 days after treatment.

Residues on tops treated at 1 1/2 lb/A ranged from <0.05 to 0.58 ppm and at 3 lb/A from 0.09 to 1.5 ppm. Residues on roots treated at 1 1/2 lb/A ranged from <0.05 to 0.08 ppm and at 3 lb/A from <0.05 to 0.21 ppm.

These limited residue data do not show any residue exceeding the proposed tolerance. However, the data are too limited to draw a conclusion on the adequacy of the tolerance. Additional residue data are needed for other growing areas to include the Rocky Mountain States, Great Plains and North Central States.

Furthermore, the submitted data are incomplete in many require areas:

1. Information is needed regarding the time between sampling and analysis.
2. Storage stability data are needed if samples were stored for a long period.
3. Additional raw data are needed, such as sample chromatograms for G.C. and standard curves for colormetric determinations.

In conclusion, the questions discussed above will have to be resolved before we can recommend for the proposed tolerance.

Sugar Beet By-products (Pulp, Molasses, Sugar)

Sugar beet pulp was prepared in the laboratory simulating commercial processing. Pulp was processed from roots treated at 1 1/2 lb and 3 lb/A with formulated linuron as prescribed. The roots were washed, ground and extracted with hot water (80°C). The extracted wet pulp was then dried at 110°F for 16 hours. 500 gram samples of sugar beet roots yielded ca 30 grams of dried pulp. The concentration factor ranged from 4.4x to 9x, averaging about 7x.

Residues in the pulp were 0.52 and 0.54 ppm in 1 1/2 lb/A treated sugar beets and 0.57 and 1.5 in 3 lb/A treated roots (1x and 2x maximum proposed rate). It is difficult from this limited data to make a reliable estimate of the residue expected in sugar beet pulp. More data are needed on pulp to make a reliable estimate of residues.

No data were submitted for residues in molasses or sugar. Data are needed to determine what, if any, residues are present in these processed commodities. The additional data requested on dried pulp, molasses and sugar should reflect the processing of beets bearing residues at or near the proposed tolerance level. Appropriate food additive tolerances should be proposed if necessary.

Meat and Milk

Sugar beet tops, pulp and molasses are considered feed items for livestock. No data were submitted with this petition on residues in meat milk poultry or eggs.

We concluded in our review of PP#6G1791/6H5135 linuron on sugar beets (9/13/76 A. Smith) that residues are likely to occur in meat of livestock (except poultry) from residues of linuron in the listed feed commodities. We reiterate that conclusion. Linuron tolerances are already established on other feed items such as corn (which has a 1 ppm tolerance) and is used as a larger percentage of the livestock diet than are sugar beets. Thus, even though we are not certain of the tolerance level needed for sugar beets, tops and by-products, we believe that the established meat tolerances are adequate to cover secondary residues resulting from the proposed use.

In addition, the topical discussion of the linuron Registration standard concludes that the established tolerances for the meat, fat and meat by-products of cattle, hogs, horses and sheep are adequate. It does suggest that the tolerances be lowered for the meat, fat and meat by-products (except liver and kidney). This lowering of the established meat tolerances will not be made an issue in this review, however. Even if the meat tolerances were to be lowered as the standard suggest, the lower meat tolerances would be adequate to cover secondary residues resulting from the proposed use.

No milk tolerance was established at the time earlier tolerances were established because it was considered that no detectable residues would result in milk from feeding the crop bearing residues at the tolerance level (see review with PP#6G1791).

The possibility of residues occurring in milk does exist since one study in which cows were fed linuron at 50 ppm for 30 days showed 0.35 ppm residue in milk (PP#356). This places the use in category 2 of 40 CFR 180.6 (a) and current policy dictates that tolerance for linuron in milk is required. The linuron Registration Standard also concludes that a tolerance is needed for milk. The petitioner should submit a milk tolerance proposal along with supporting data and methodology. The IR-4 should consult with Dupont on this question.

With respect to poultry tissue and eggs, the Registration Standard concludes that, based on poultry feeding data, no tolerance is needed on poultry tissue and eggs from the feeding of 0.75 ppm linuron in the poultry diet. It is not expected that feeding sugar beet molasses derived from linuron treated beets at 4% of the diet would alter this conclusion.

Other Considerations

There is no Codex tolerance proposal for linuron on sugar at step 6 or above. The "International Residue Limit Status" sheet is attached.

TS-769:RCB:JMayes:vg:CM#2:Rm810:X77377:11/2/82
cc: RF, Circ., Mayes, Thompson, FDA, TOX, EEB, EFB, PP#2E2706/2H5354
RDI: Quick, 10/29/82; Schmitt, 10/29/82